Università degli Studi di Ferrara

Machine-Learned Interatomic Potentials as forcefields for Molecular Dynamics simulations of Nanoconfined Supercritical Water

Laurea Magistrale in Scienze Chimiche
Anno accademico 2024/2025

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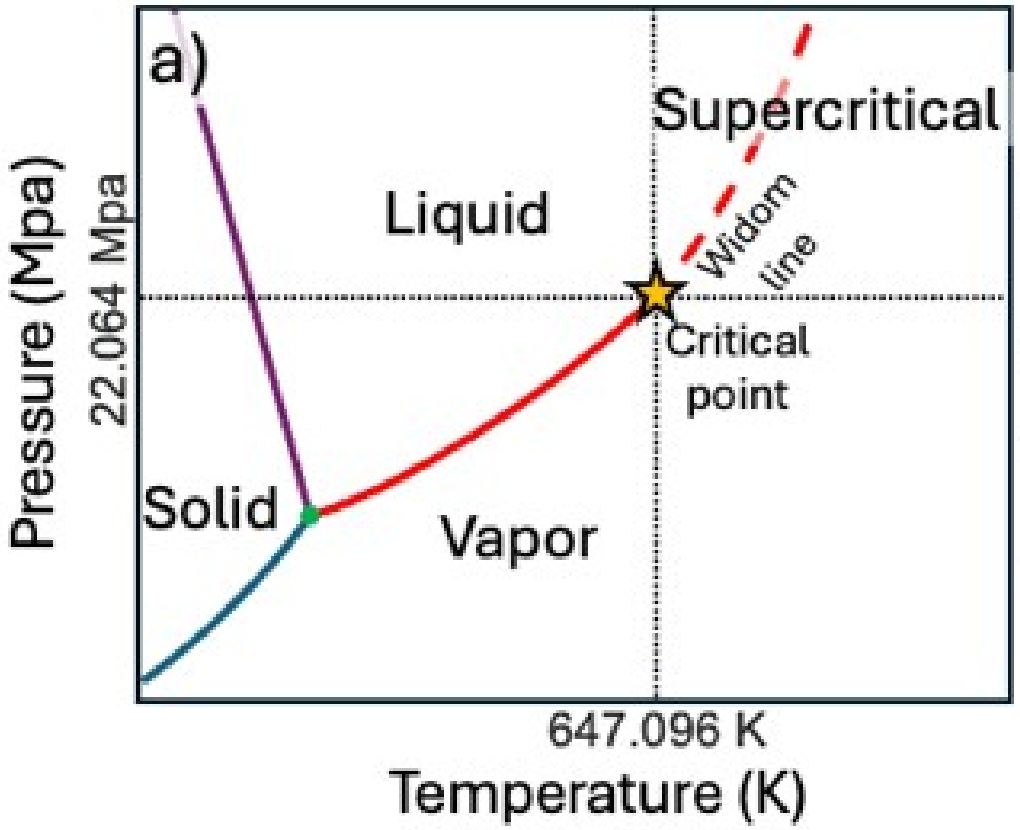
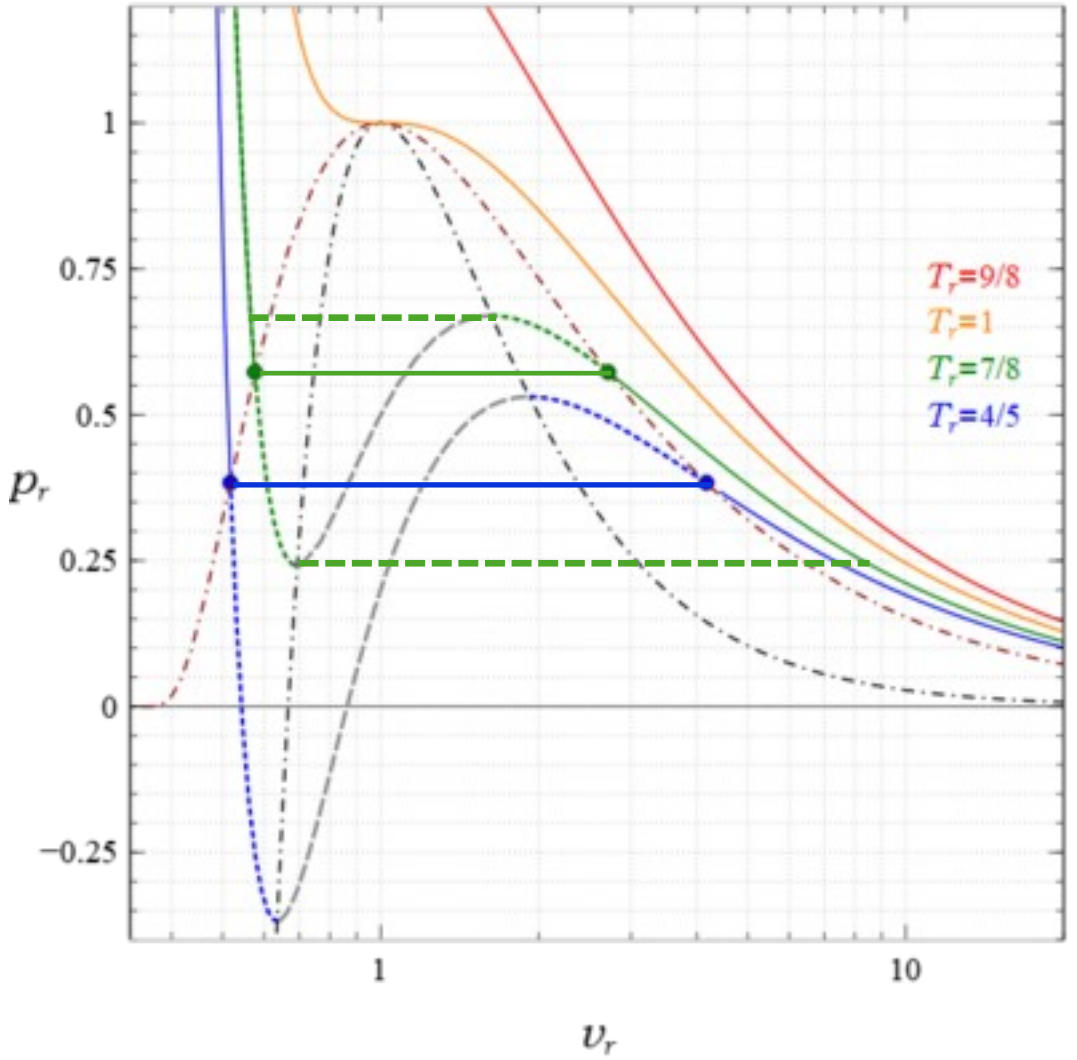
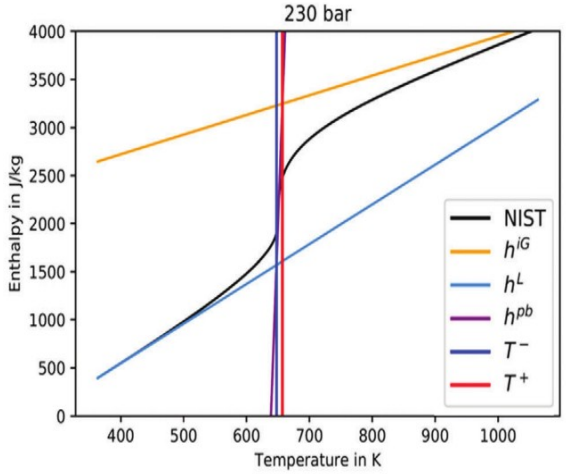
Relatore: Prof. Simone Meloni

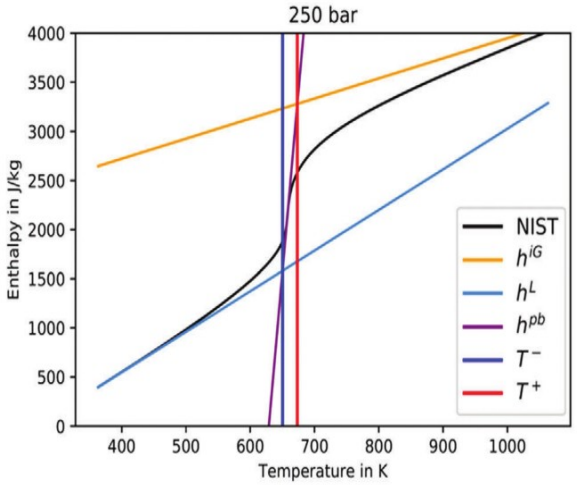
Phase diagram and transition of bulk water

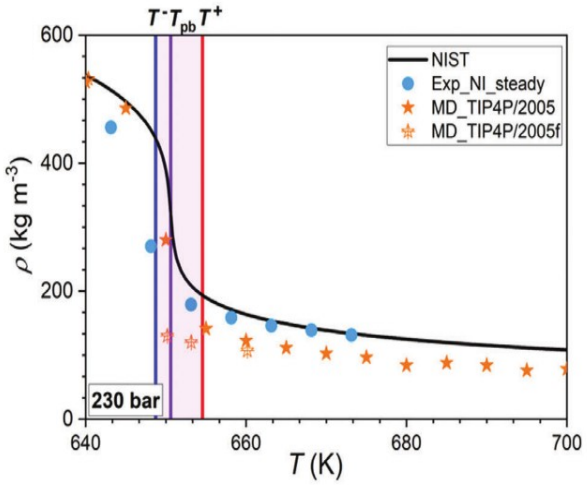


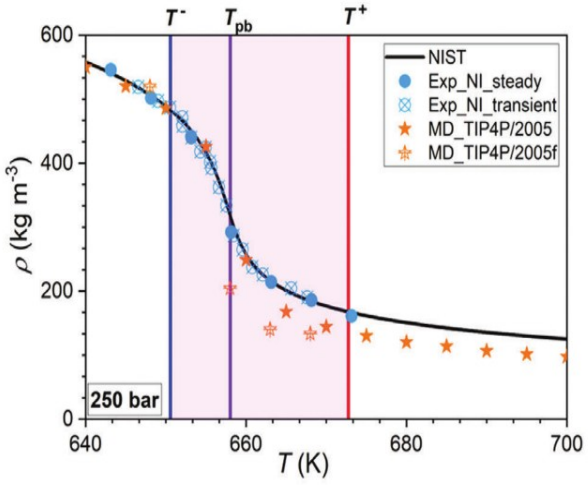


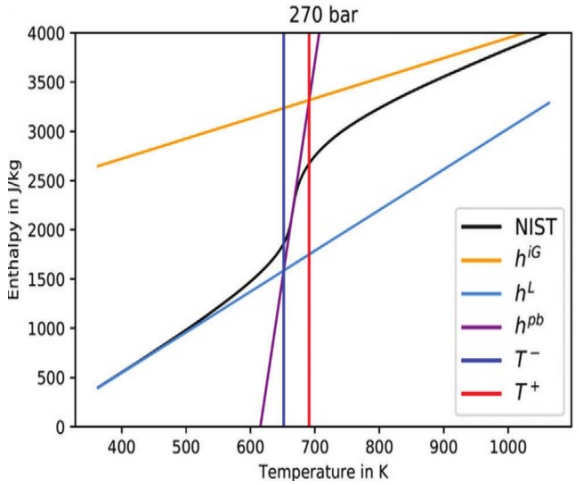
Supercritical phase transitions

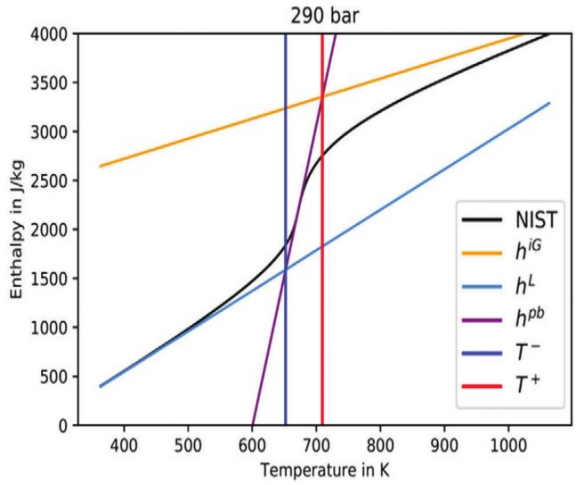


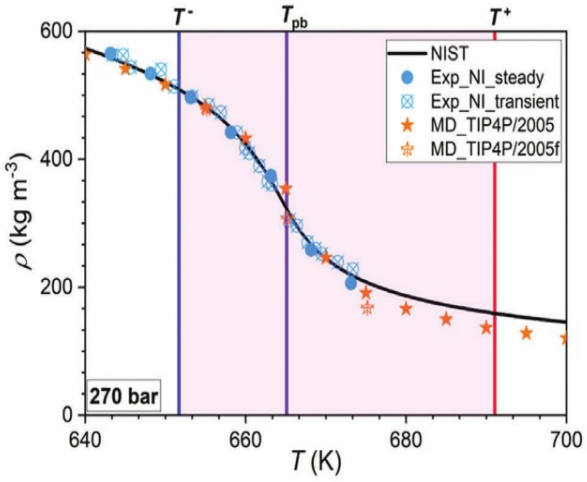


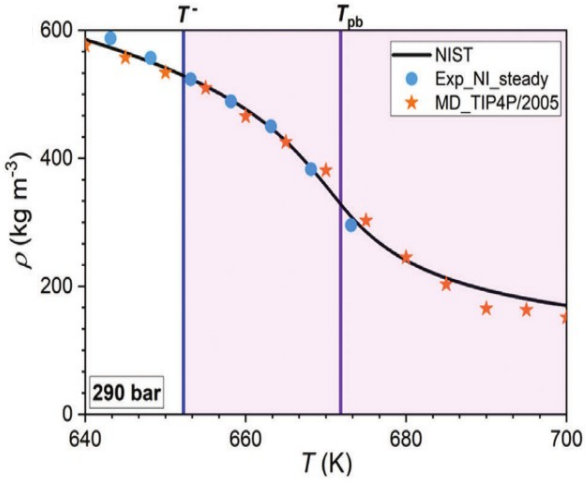




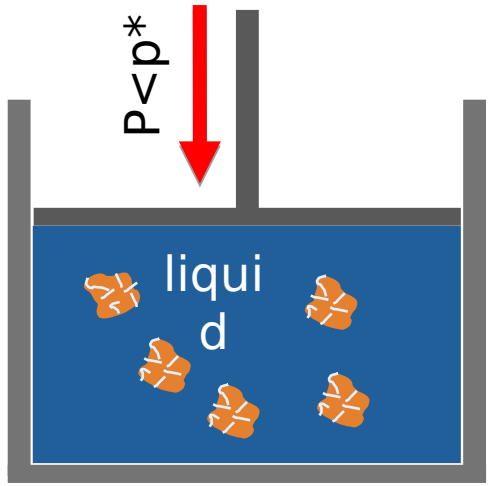






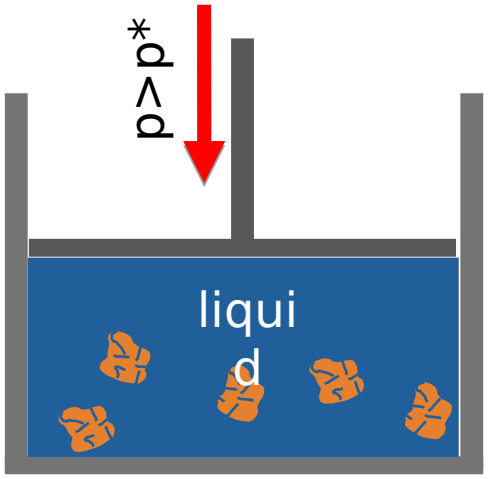


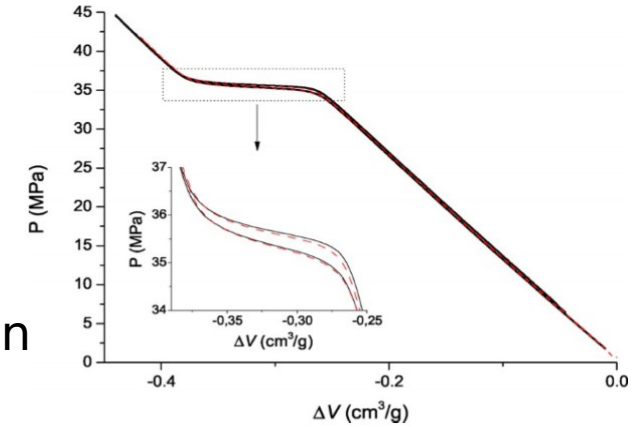
Nanoconfinement of water: capillary condensation and evaporation

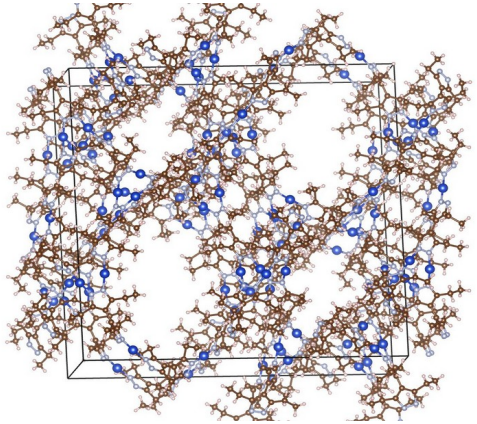


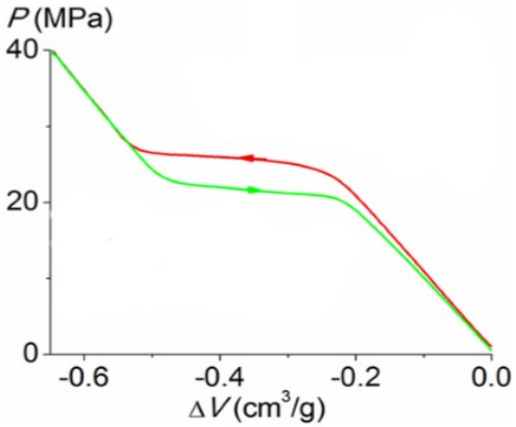
Extrusion

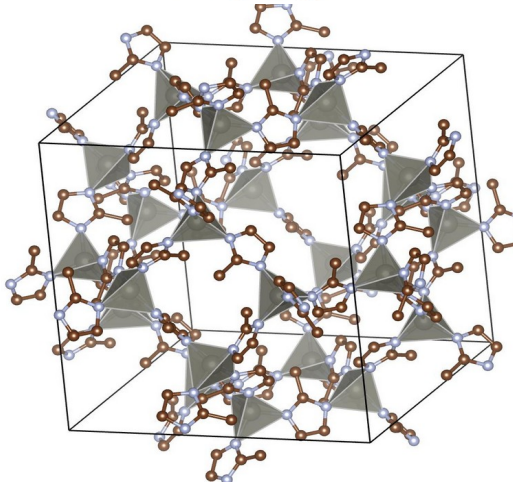
Intrusion

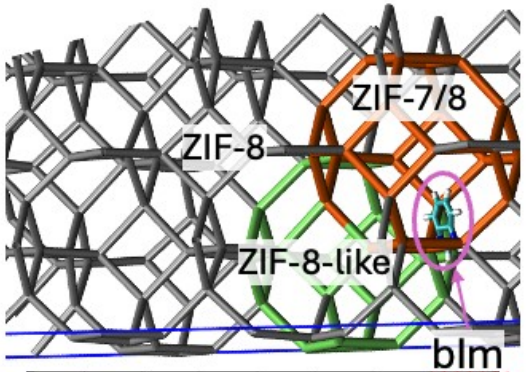


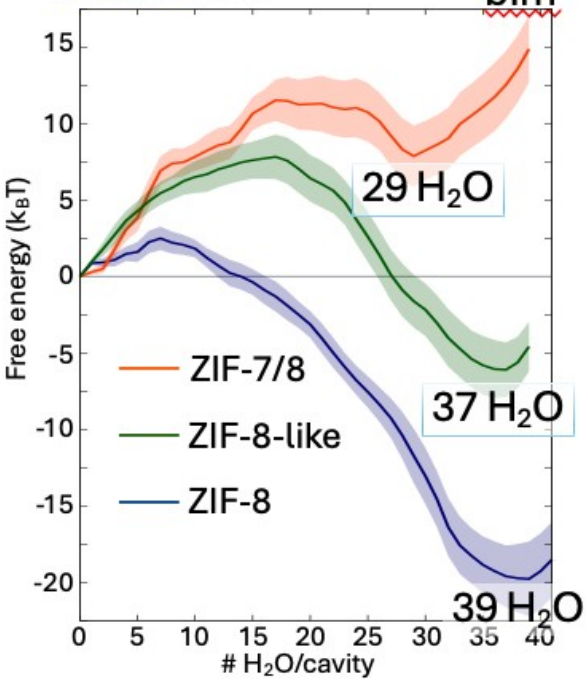




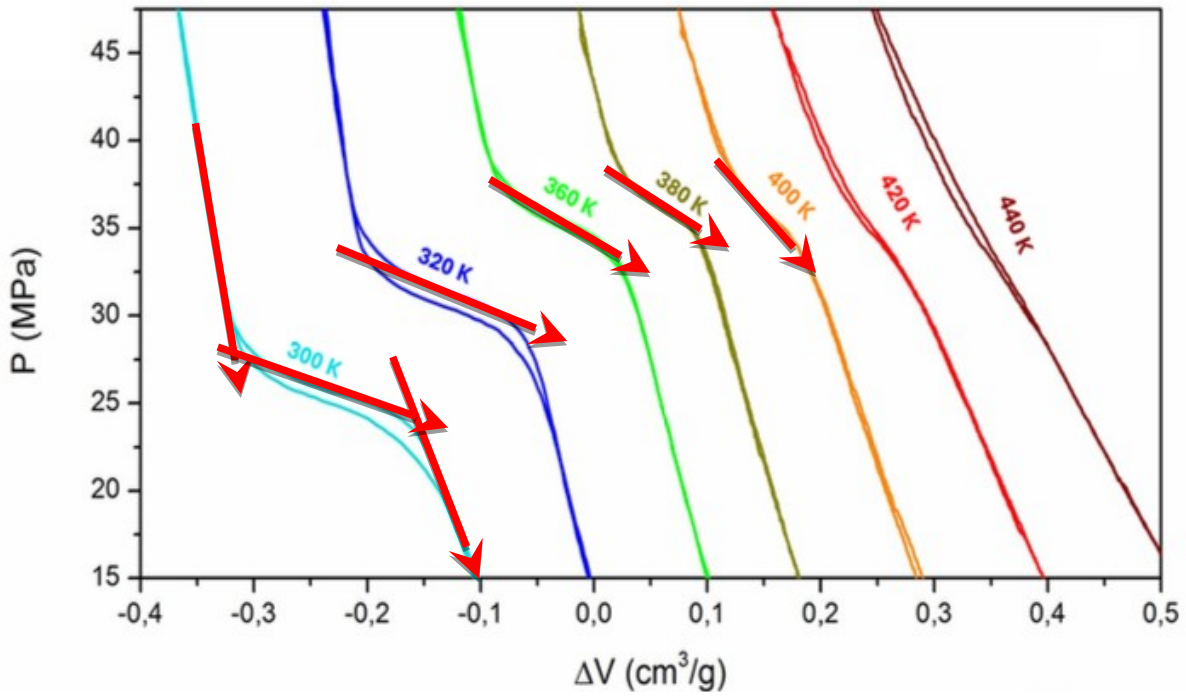


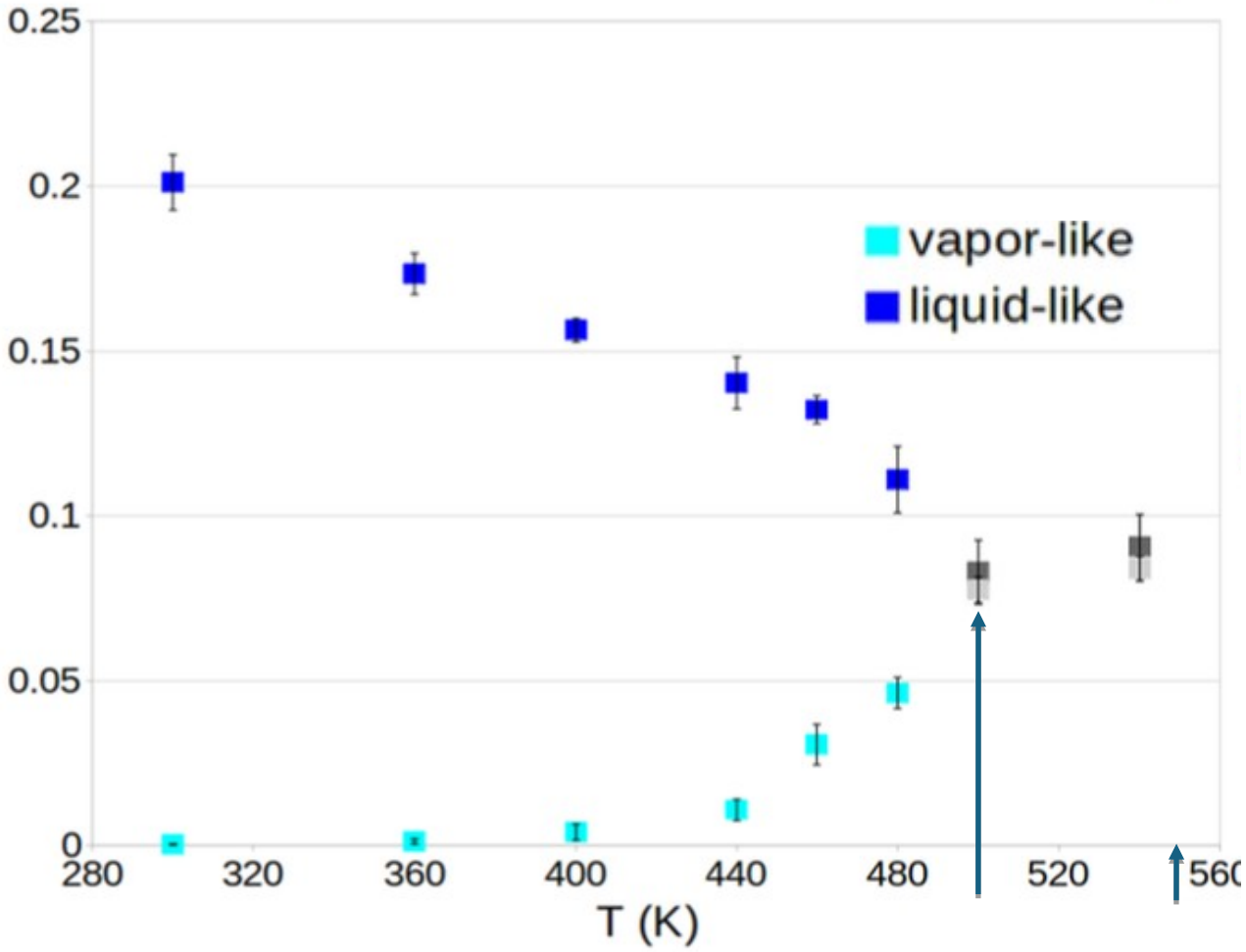




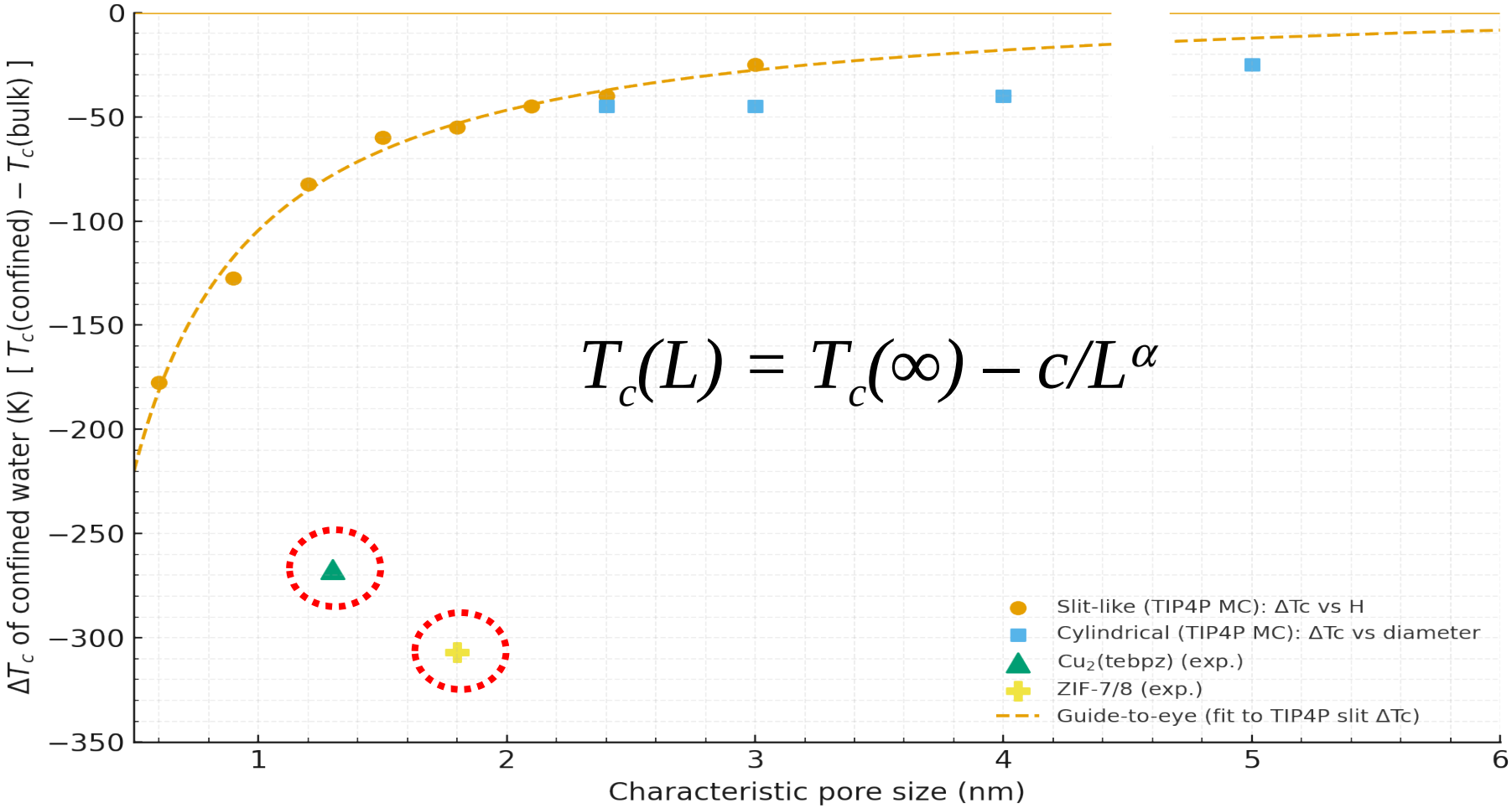


Mild, confined supercritical water

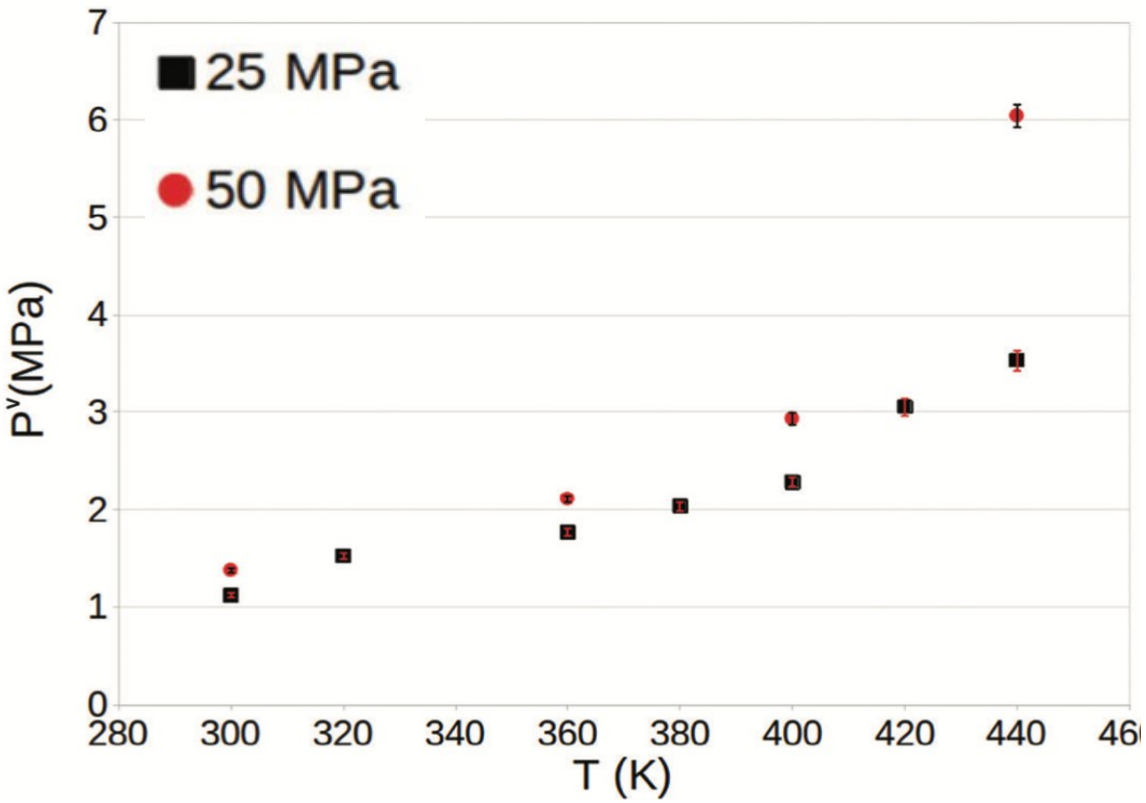


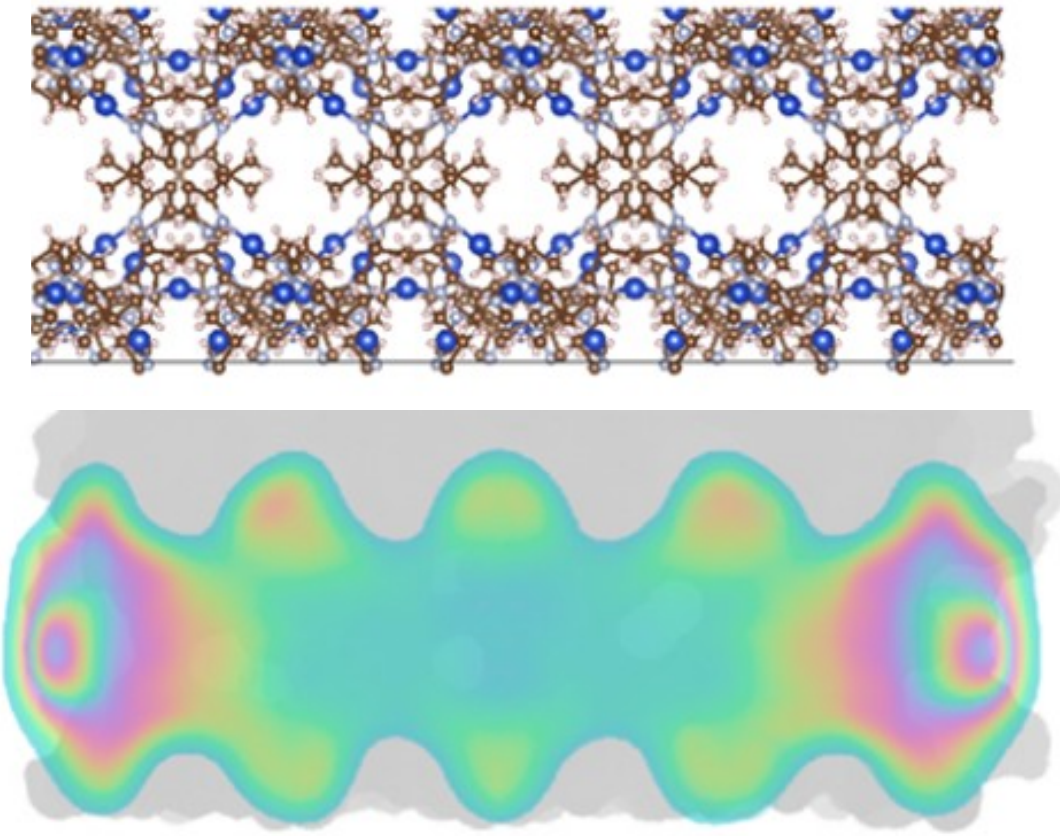


Effect of confinement on Tc

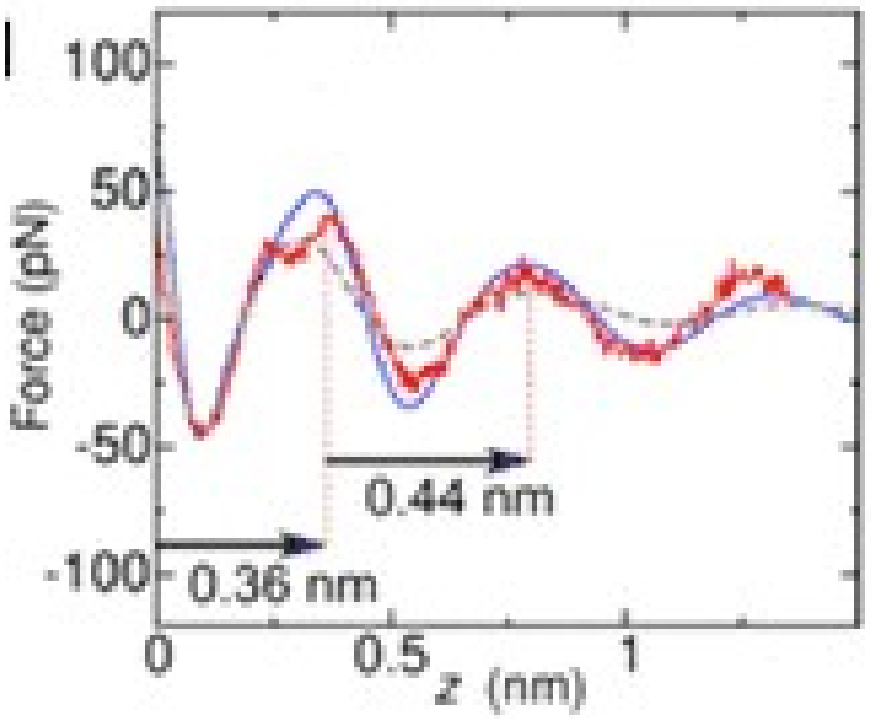


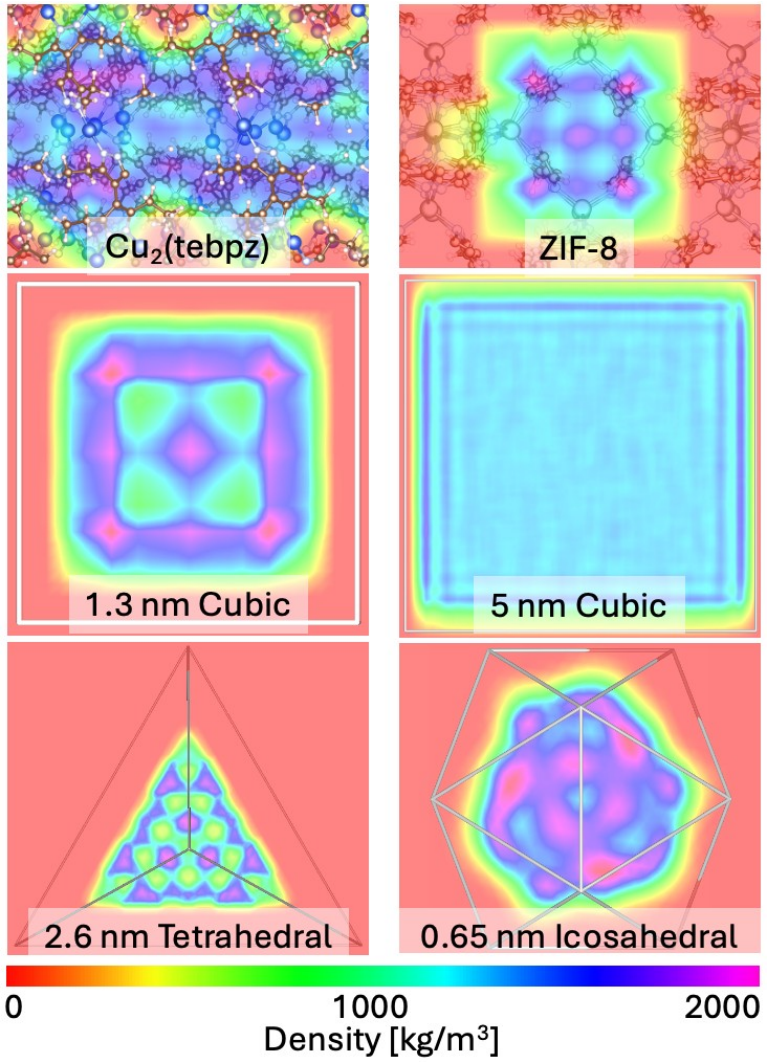
Effect of confinement on Tc: high vapor pressure





Effect of confinement on Tc: hydrophobic forces and geometrical features





Experiments *in silico*: Molecular Dynamics

$$\langle A \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(t)dt \approx \frac{1}{M} \sum_{i=1}^{M} A(t_i)$$

$$\mathcal{H}_{\mathrm{MTTK}} = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{q}) + \frac{p_\xi^2}{2Q} + gk_BT\xi + \frac{p_\eta^2}{2W} + 3Nk_BT\eta + P_{\mathrm{ext}}V$$

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m_i} + \eta\,\mathbf{q}_i$$

$$\dot{\mathbf{p}}_i = -\nabla_{\mathbf{q}_i} V - (\xi + \eta)\,\mathbf{p}_i$$

$$\dot{V} = 3V\eta$$

$$\dot{\eta} = \frac{1}{W}\left(P - P_{\mathrm{ext}}\right)$$

$$\dot{\xi} = \frac{1}{Q}\left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - 3Nk_BT\right)$$

Interatomic potentials from electronic structures

Hellmann-Feynman theorem:

$$\mathbf{F}_A = -\frac{\partial E(\{\mathbf{R}_A\})}{\partial \mathbf{R}_A} = -\left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \mathbf{R}_A} \right| \Psi \right\rangle$$

$$\hat{H}(\{\mathbf{r}_i\};\{\mathbf{R}_A\})\,\Psi(\{\mathbf{r}_i\};\{\mathbf{R}_A\}) = E(\{\mathbf{R}_A\})\,\Psi(\{\mathbf{r}_i\};\{\mathbf{R}_A\})$$

$$\hat{H} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{\text{ext}}(\mathbf{r}_i;\{\mathbf{R}_A\})$$

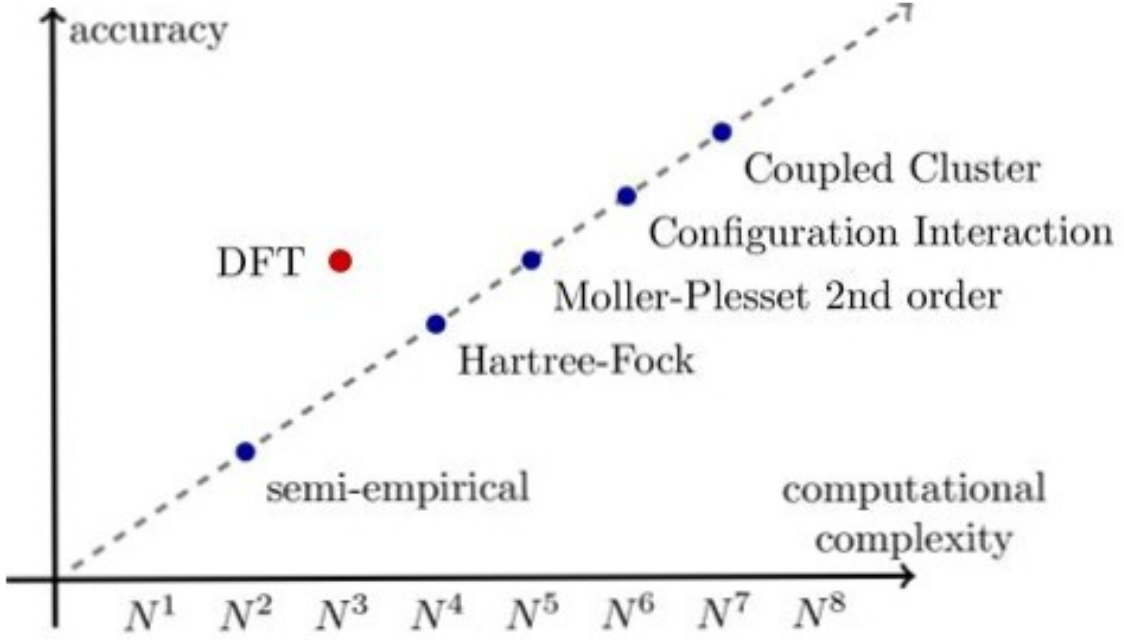
Electronic structure approximation: Density Functional Theory

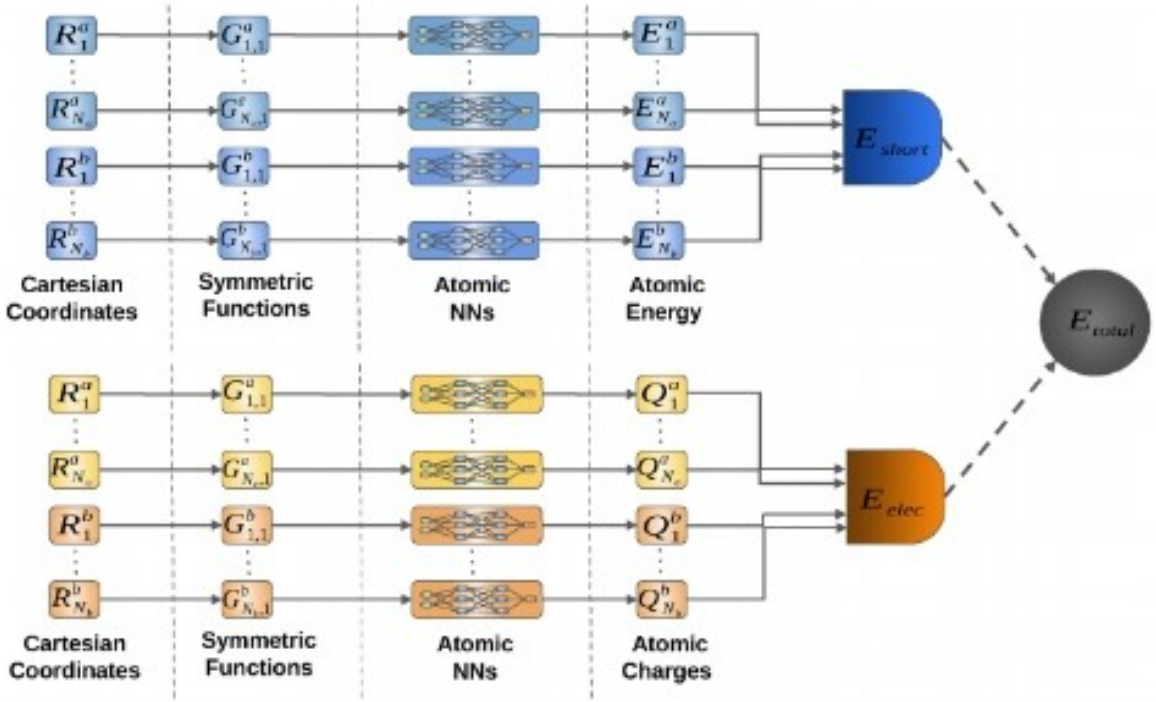
$$\rho(\mathbf{r}) = \sum_{i}^{\mathrm{occ}} |\psi_i(\mathbf{r})|^2. \qquad \left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{\mathrm{eff}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\,\psi_i(\mathbf{r}),$$

$$V_{\mathrm{eff}}(\mathbf{r}) = V_{\mathrm{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + V_{\mathrm{XC}}[\rho](\mathbf{r}), \quad V_{\mathrm{XC}}[\rho](\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}[\rho]}{\delta\rho(\mathbf{r})}.$$

$$E_{\mathrm{KS}}[\rho] = T_s[\rho] + E_{\mathrm{ext}}[\rho] + E_{\mathrm{H}}[\rho] + E_{\mathrm{XC}}[\rho],$$

A step further from Classical an Ab Initio MD:ML Interatomic Potentials





MLIP: MACE foundation models

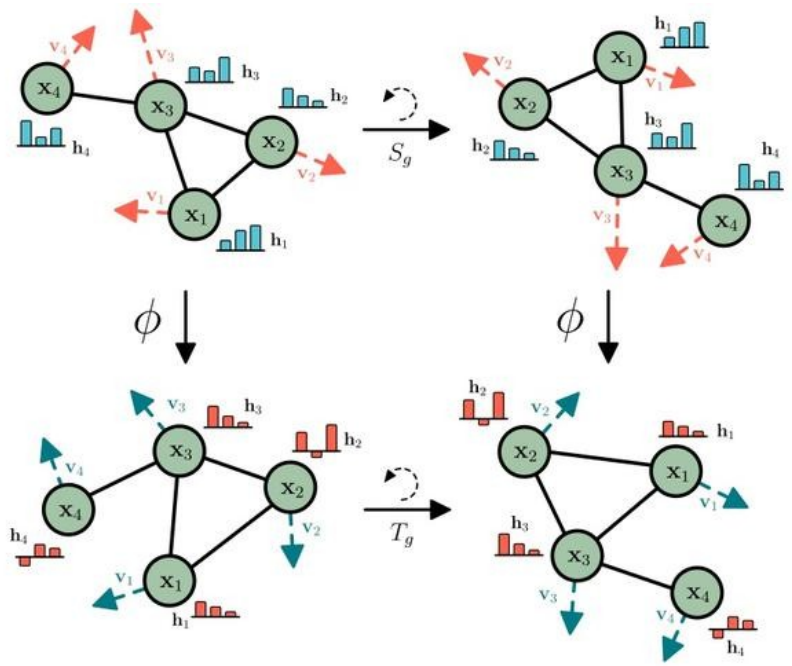
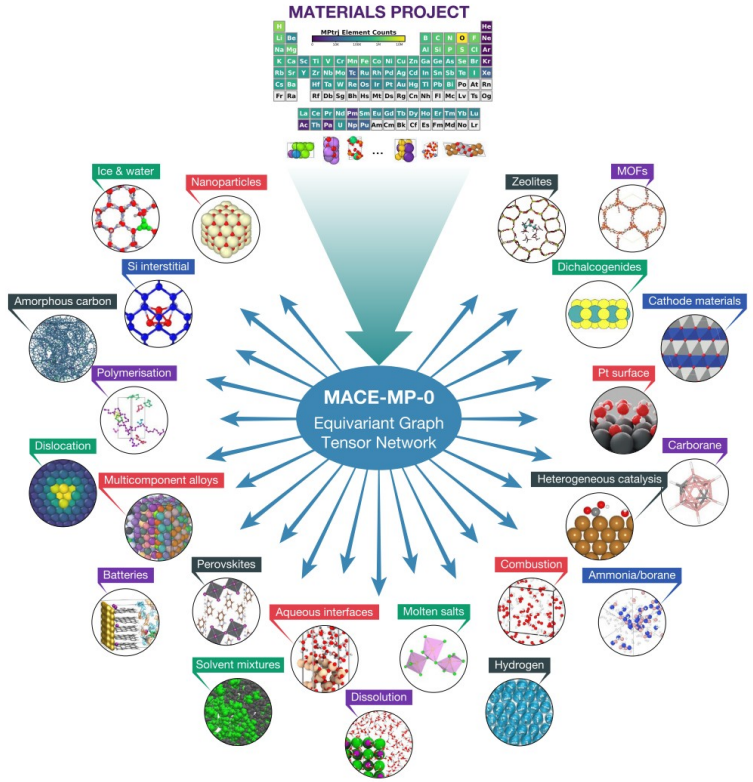


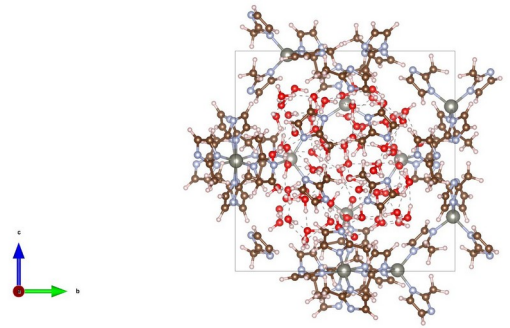
Figure 1. Example of rotation equivariance on a graph with a graph neural network ϕ

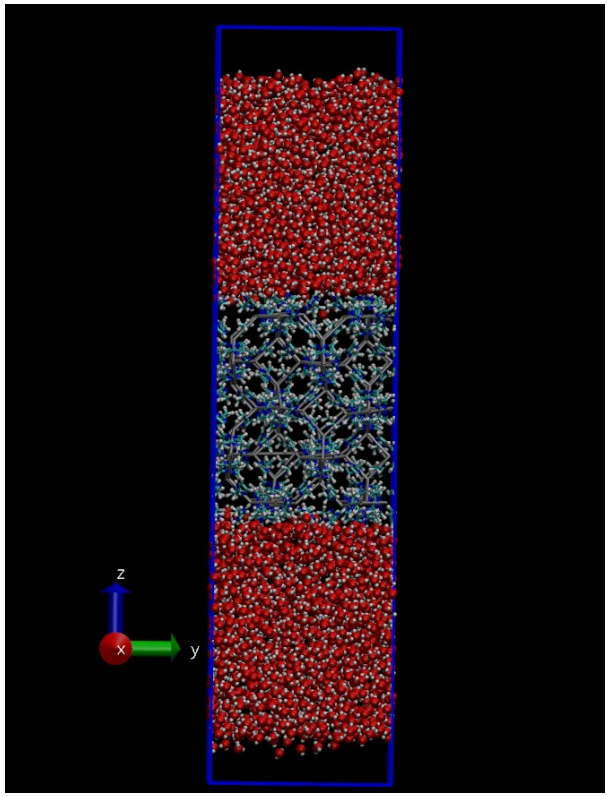
$$m_{ij;L,M}^{(t)} = \sum_{\ell_1,m_1} \sum_{\ell_2,m_2} C_{\ell_1 m_1,\ell_2 m_2}^{LM} \left[h_{j;\ell_1,m_1}^{(t)}\right]^{\top} \cdot \mathcal{W}_{\ell_1\ell_2 L}^{(t)} \cdot Y_{\ell_2}^{m_2}(\hat{\mathbf{r}}_{ij}) \cdot F_{\ell_1\ell_2 L}^{(t)}(r_{ij})$$

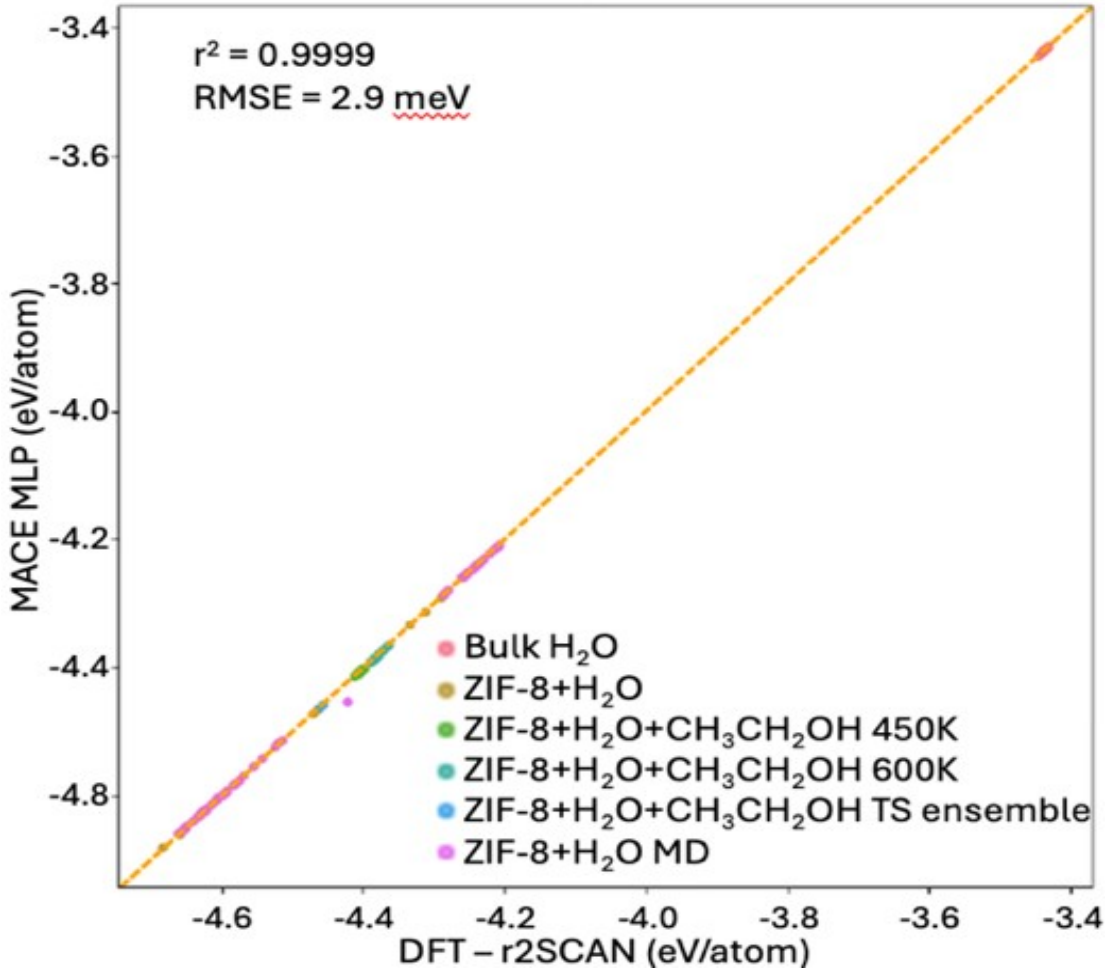


Training of MLIP: generation of datasets

DFT-curated dataset to sample the relevant configurational space







Training of MLIP: representing bulk water

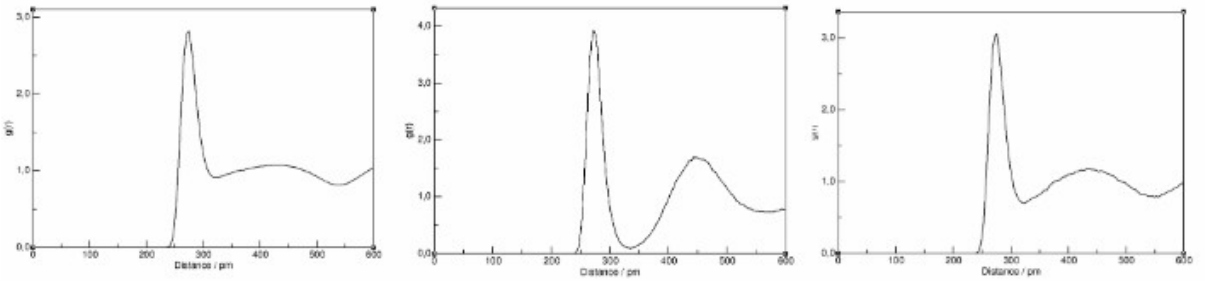
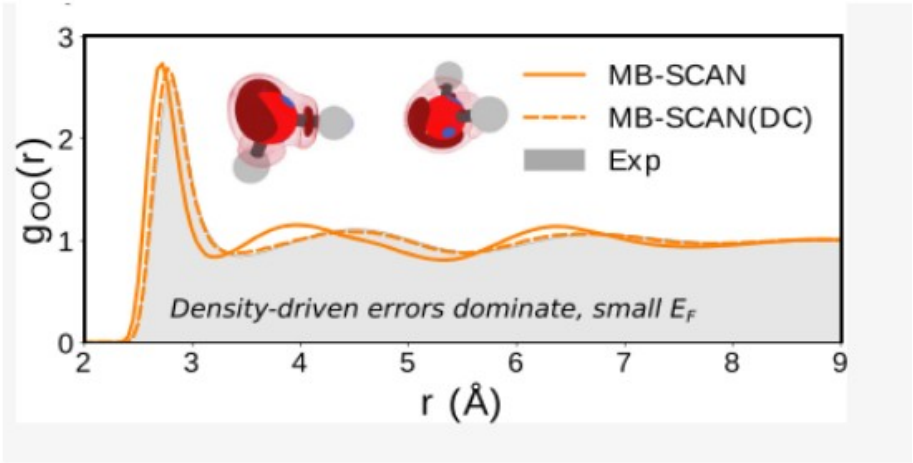
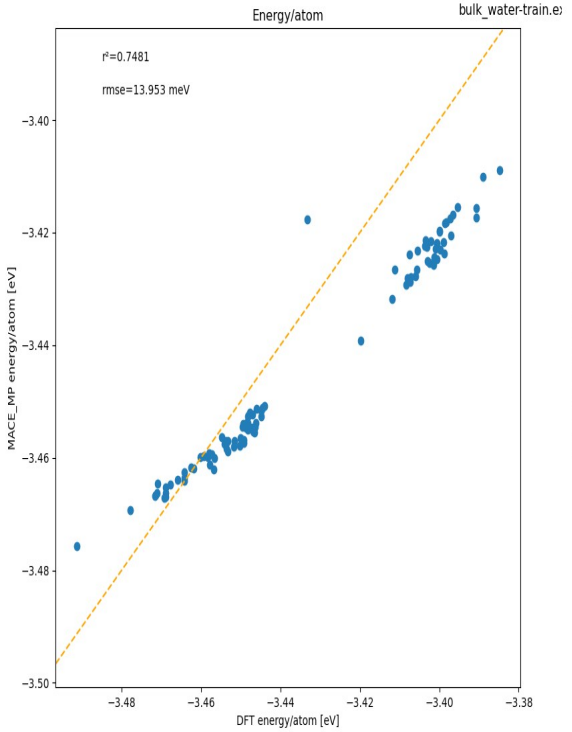
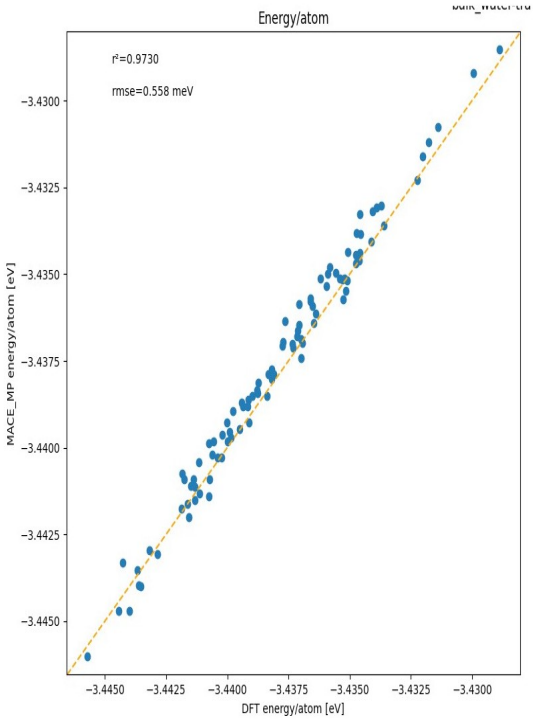


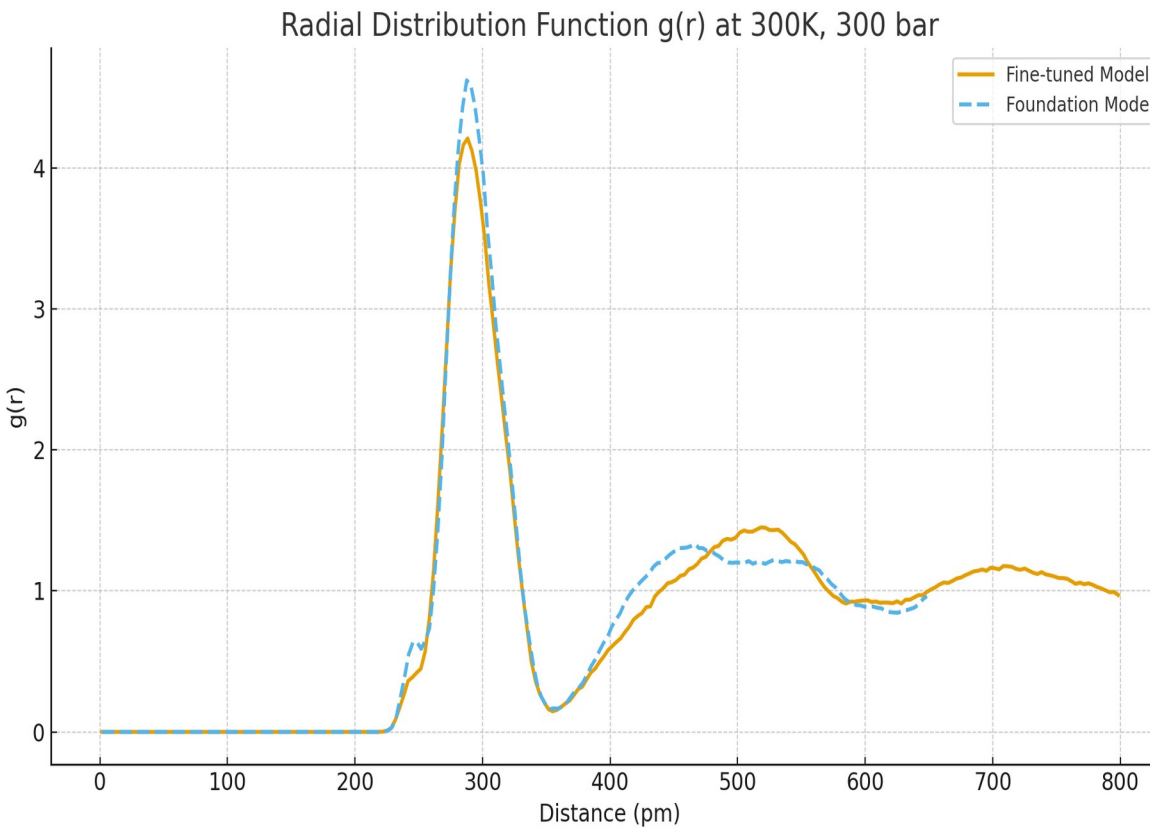
Figure 4.3: g(r) of O-O from foundation models:**left** MPA(PBE+U); **centre** MATPES(PBE); **right**MATPES(r2SCAN)

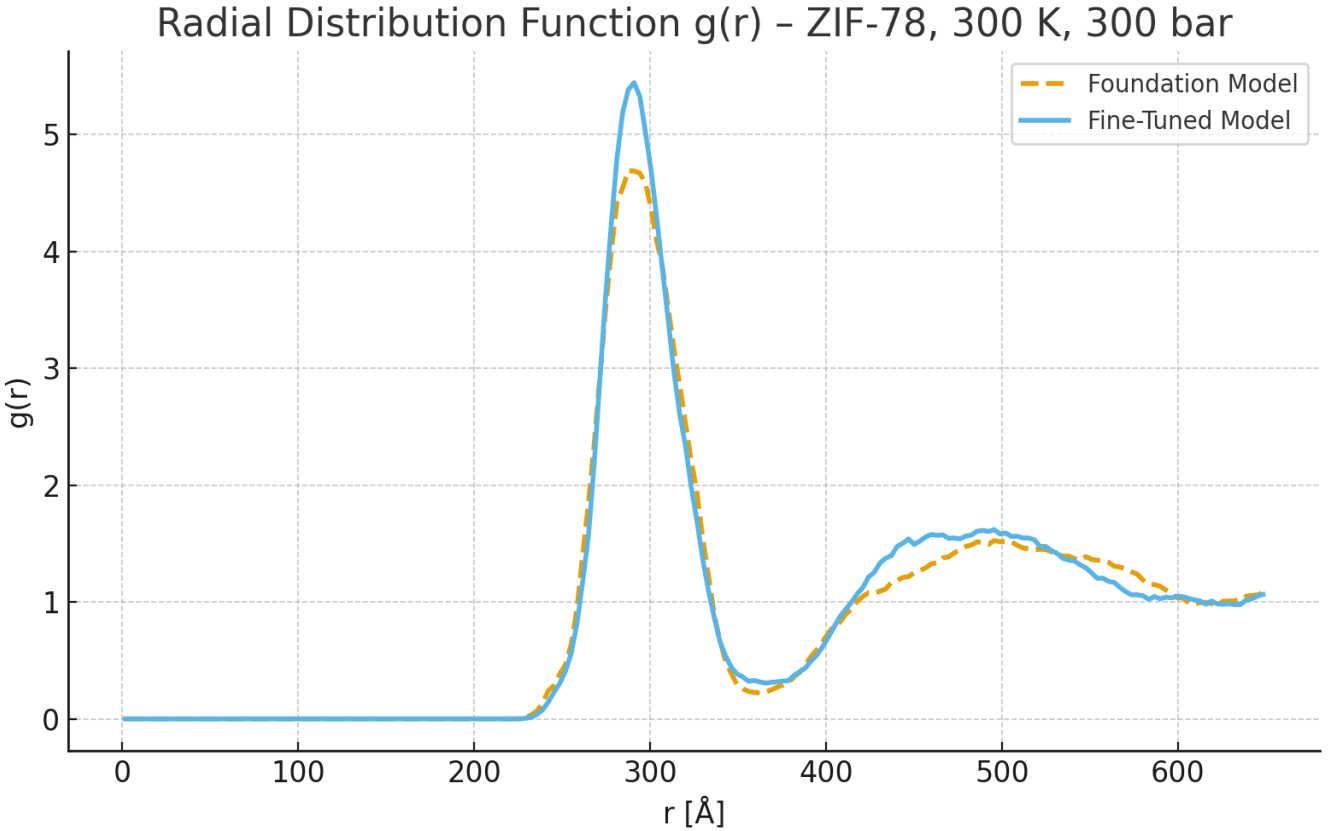






Training of MLIP: representing confined water





Conclusions

Foundation models need fine-tuning to represent water

Accuracy at AIMD level with CMD computational cost

More reliable quantitative analysis of confined water and free energy profile

Flexible potentials to capture physicochemical properties of confined water